

# Organometallic ferrocenyl dendrimers: synthesis, characterization and redox properties

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A series of dendritic poly(aryl ether)s containing 3, 6, 12 and 24 ferrocene functionalities located exclusively at the peripheries of the dendritic structures have been synthesized using the stepwise convergent approach. The structures of these dendrimers have been characterized using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Cyclic and normal pulse voltammetric studies indicate that the ferrocenyl moieties located on the outer surfaces of these dendrimers are non-interacting redox centres, are electrochemically equivalent, and are oxidizable at the same potential. The results of controlled-potential coulometric oxidation show that nearly all the ferrocene residues in the dendrimers are accessible to electron transfers in electrode reactions.

Macromolecular materials with skeletons of transition-metal atoms in close proximity are attracting increasing attention because of their potentially interesting electrical, redox and optical characteristics. Among the organotransition-metal complexes, ferrocene has been shown to have excellent thermal and photochemical stability, and to undergo a facile and reversible one-electron oxidation to ferrocenium cation; the reaction leads to a marked change in electrical and spectroscopic properties and may be effected chemically, electrochemically or photochemically. Ferrocenyl-based polymers have been used in chemical modification of electrodes, in the construction of amperometric biosensors, and in the area of non-linear optical materials.<sup>1</sup>

Recently, dendritic macromolecules have received considerable attention because of their unique hyperbranched polymeric structure and well defined three-dimensional architectures.<sup>2</sup> These dendritic macromolecules are characterized by a central polyfunctional core, from which arise successive layers of monomer units with branches occurring at each monomer unit.<sup>3</sup> This results in a nearly entanglement-free hyperbranched structure that may adopt a spherical shape, the periphery of which consists of a large number of chain ends or surface functional groups.<sup>4</sup> This unique macromolecular architecture allows precise control of molecule size, as well as of the disposition of the desired functionalities. The synthesis of well defined, highly branched macromolecules possessing functional components on their exterior surfaces, within their dendritic branches, and at their interior cores, giving rise to new materials with desirable properties has sparked much interest.<sup>4–6</sup> In this paper, we report full details on the synthesis, characterizations and redox behaviour of a family of dendritic poly(aryl ether)s that were synthesized using a stepwise convergent approach,<sup>7</sup> and possess ferrocene functional groups located exclusively at the peripheries of their dendritic structures.

## Experimental

### Materials

Acetone was distilled from  $\text{CaSO}_4$ . Benzene was distilled from  $\text{CaH}_2$ . Tetrahydrofuran (THF) was distilled from Na/K alloy and benzophenone. *n*-Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was prepared as described previously,<sup>8</sup> and was purified by recrystallization three times from ethyl acetate and dried *in vacuo* at 60 °C. 3-Ferrocenylpropanol<sup>9</sup> and 3,5-dihydroxybenzyl alcohol<sup>10</sup> were synthesized according to the

reported procedures. Other commercially available chemicals were reagent grade and were used as purchased.

### 3-Bromopropylferrocene (Fc-G0-Br)<sup>11</sup>

To a mixture of 3-ferrocenylpropanol (5.43 g, 22.3 mmol) and carbon tetrabromide (14.63 g, 44.6 mmol) in 10 ml of THF was added triphenylphosphine (11.53 g, 44 mmol). The reaction mixture was stirred at room temperature under nitrogen for 1 h. The resulting mixture was then poured into water and extracted with diethyl ether. The extract was dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:10 ethyl acetate–hexane, to give 4.67 g (69%) of Fc-G0-Br as an orange oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.04 (m, 2H,  $\text{CH}_2$ ), 2.50 (t, 2H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.42 (t, 2H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.07 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.10 (s, 5H,  $\text{C}_5\text{H}_5$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.91 ( $\text{CH}_2$ ), 33.63 ( $\text{CH}_2\text{Br}$ ), 33.91 ( $\text{CpCH}_2$ ), 67.36, 6814 ( $\text{C}_5\text{H}_4$ ), 68.57 ( $\text{C}_5\text{H}_5$ ), 88.25 ( $\text{C}_5\text{H}_4$ ).

### General procedure for the synthesis of Fc-Gx-OH ( $x = 1, 2, 3$ )

A mixture of the appropriate Fc-Gx-Br ( $x = 0, 1, 2$ ) (2 equiv.), 3,5-dihydroxybenzyl alcohol (1 equiv.), potassium carbonate, (3.5 equiv.) and 18-crown-6 (0.2 equiv.) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool, added to water and extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$ ). The combined extracts were dried over  $\text{MgSO}_4$  and evaporated to dryness. The crude product was purified as outlined in the following text.

### General procedure for the synthesis of Fc-Gx-Br ( $x = 1, 2, 3$ )<sup>12</sup>

To a solution of Fc-Gx-OH ( $x = 1, 2, 3$ ) (1 equiv.) in benzene was added dropwise  $\text{PBr}_3$  (0.4 equiv.). The reaction mixture was stirred at room temperature under nitrogen for 4 h. For the latter generation ( $x = 3$ ), larger excesses of  $\text{PBr}_3$  were required to force the reaction to completion.  $\text{PBr}_3$  was added in 0.4 equiv. amounts at hourly intervals until TLC showed no starting material. The mixture was then added to water, neutralized with saturated aqueous  $\text{NaHCO}_3$ , and extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$ ). The combined extracts were dried over  $\text{MgSO}_4$  and evaporated to dryness. The crude product was purified as outlined in the following text.

### Fc-G1-OH

This was prepared from Fc-G0-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 2:5 ethyl acetate–hexane,

to give Fc-G1-OH (79%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 4H,  $\text{CH}_2$ ), 2.51 (t, 4H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.96 (t, 4H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.06 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.62 (d, 2H,  $J$  = 4.8 Hz,  $\text{CH}_2\text{OH}$ ), 6.40 (t, 1H,  $J$  = 2.0 Hz, ArH), 6.52 (d, 2H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.50 ( $\text{CpCH}_2$ ), 65.37, 67.27 ( $\text{CH}_2\text{O}$ ), 67.27, 68.14 ( $\text{C}_5\text{H}_4$ ), 68.55 ( $\text{C}_5\text{H}_5$ ), 88.19 ( $\text{C}_5\text{H}_4$ ), 100.57, 105.12, 143.26, 160.41 (ArC).

### Fc-G1-Br

This was prepared from Fc-G1-OH and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:5 ethyl acetate–hexane to give Fc-G1-Br (85%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 4H,  $\text{CH}_2$ ), 2.51 (t, 4H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.95 (t, 4H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.06 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.06 (m, 4H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.41 (s, 2H,  $J$  = 4.8 Hz,  $\text{CH}_2\text{Br}$ ), 6.39 (t, 1H,  $J$  = 2.0 Hz, ArH), 6.52 (d, 2H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.44 ( $\text{CpCH}_2$ ), 33.76 ( $\text{CH}_2\text{Br}$ ), 67.27 ( $\text{CH}_2\text{O}$ ), 67.21, 68.09 ( $\text{C}_5\text{H}_4$ ), 68.49 ( $\text{C}_5\text{H}_5$ ), 99.10 ( $\text{C}_5\text{H}_4$ ), 101.42, 139.59, 160.27 (ArC).

### Fc-G2-OH

This was prepared from Fc-G1-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:3 hexane–chloroform to give Fc-G2-OH (85%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 8H,  $\text{CH}_2$ ), 2.51 (t, 8H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.96 (t, 8H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.05 (m, 8H,  $\text{C}_5\text{H}_5$ ), 4.08 (m, 8H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 20H,  $\text{C}_5\text{H}_5$ ), 4.62 (d, 2H,  $J$  = 4.8 Hz,  $\text{CH}_2\text{OH}$ ), 4.96 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 6.42 (t, 2H,  $J$  = 2.0 Hz, ArH), 6.54 (t, 1H,  $J$  = 2 Hz, ArH), 6.57 (d, 4H,  $J$  = 2.0 Hz, ArH), 6.61 (d, 2H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.50 ( $\text{CpCH}_2$ ), 65.27 ( $\text{CH}_2\text{O}$ ), 67.23 ( $\text{C}_5\text{H}_4$ ), 67.41 ( $\text{CH}_2\text{O}$ ), 68.41 ( $\text{C}_5\text{H}_4$ ), 68.52 ( $\text{C}_5\text{H}_5$ ), 70.03 ( $\text{CH}_2\text{O}$ ), 88.20 ( $\text{C}_5\text{H}_4$ ), 100.80, 101.27, 105.65, 105.73, 139.03, 143.37, 160.08, 160.36 (ArC).

### Fc-G2-Br

This was prepared from Fc-G2-OH and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 2:3 hexane–chloroform to give Fc-G2-Br (44%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 8H,  $\text{CH}_2$ ), 2.51 (t, 8H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.96 (t, 8H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.07 (m, 8H,  $\text{C}_5\text{H}_4$ ), 4.09 (m, 8H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 20H,  $\text{C}_5\text{H}_5$ ), 4.42 (s, 2H,  $\text{CH}_2\text{Br}$ ), 4.95 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 6.43 (t, 2H,  $J$  = 2.0 Hz, ArH), 6.55 (t, 1H,  $J$  = 2.0 Hz, ArH), 6.57 (d, 2H,  $J$  = 2.0 Hz, ArH), 6.64 (d, 2H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.47 ( $\text{CpCH}_2$ ), 33.65 ( $\text{CH}_2\text{Br}$ ), 67.27 ( $\text{C}_5\text{H}_4$ ), 67.33 ( $\text{CH}_2\text{O}$ ), 68.14 ( $\text{C}_5\text{H}_4$ ), 68.58 ( $\text{C}_5\text{H}_5$ ), 70.12 ( $\text{CH}_2\text{O}$ ), 88.25 ( $\text{C}_5\text{H}_4$ ), 100.89, 102.17, 105.78, 108.09, 138.80, 139.70, 159.98, 160.39 (ArC).

### Fc-G3-OH

This was prepared from Fc-G2-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:3 hexane–chloroform, to give Fc-G3-OH (63%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.97 (m, 16H,  $\text{CH}_2$ ), 2.51 (t, 16H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.95 (t, 16H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.05 (m, 16H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 16H,  $\text{C}_5\text{H}_4$ ), 4.10 (s, 40H,  $\text{C}_5\text{H}_5$ ), 4.61 (d, 2H,  $J$  = 4.8 Hz,  $\text{CH}_2\text{OH}$ ), 4.96 (s, 8H,  $\text{ArCH}_2\text{O}$ ), 4.97 (s, 4H,  $\text{ArCH}_2\text{O}$ ), 6.42 (t, 4H,  $J$  = 2.0 Hz, ArH), 6.54 (m, 3H, ArH), 6.57 (d, 8H,  $J$  = 2.0 Hz, ArH), 6.60 (d, 2H,  $J$  = 2.0 Hz, ArH), 6.68 (d, 4H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.47 ( $\text{CpCH}_2$ ), 65.23 ( $\text{CH}_2\text{O}$ ), 67.27 ( $\text{C}_5\text{H}_4$ ), 67.33 ( $\text{CH}_2\text{O}$ ), 67.74 ( $\text{C}_5\text{H}_4$ ), 68.55 ( $\text{C}_5\text{H}_5$ ), 69.95, 70.10 ( $\text{CH}_2\text{O}$ ), 88.25 ( $\text{C}_5\text{H}_5$ ), 100.86, 101.21, 101.56, 105.67, 105.79, 106.31, 138.97, 139.18, 143.37, 160.01, 160.07, 160.36 (ArC).

### Fc-G3-Br

This was prepared from Fc-G3-OH and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 2:3 hexane–chloroform

to give Fc-G3-Br (24%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 16H,  $\text{CH}_2$ ), 2.51 (t, 16H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.96 (t, 16H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.07 (m, 16H,  $\text{C}_5\text{H}_4$ ), 4.09 (m, 16H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 40H,  $\text{C}_5\text{H}_5$ ), 4.40 (s, 2H,  $\text{CH}_2\text{Br}$ ), 4.95 (s, 12H, ArCH<sub>2</sub>O), 6.42 (t, 4H,  $J$  = 2.0 Hz, ArH), 6.54 (m, 3H, ArH), 6.57 (d, 8H,  $J$  = 2.0 Hz, ArH), 6.60 (d, 2H,  $J$  = 2.0 Hz, ArH), 6.68 (d, 4H,  $J$  = 2.0 Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.47 ( $\text{CpCH}_2$ ), 33.59 ( $\text{CH}_2\text{Br}$ ), 67.27 ( $\text{C}_5\text{H}_4$ ), 67.33, 67.71, ( $\text{CH}_2\text{O}$ ), 67.74 ( $\text{C}_5\text{H}_4$ ), 68.55 ( $\text{C}_5\text{H}_5$ ), 70.10 ( $\text{CH}_2\text{O}$ ), 88.25 ( $\text{C}_5\text{H}_4$ ), 100.86, 101.62, 102.15, 105.75, 106.40, 108.12, 138.97, 159.92, 160.10, 160.36 (ArC).

### General procedure for the synthesis of dendritic molecules

A mixture of Fc-Gx-Br ( $x = 0, 1, 2, 3$ ) (3 equiv.), 1,1,1-tris(4-hydroxyphenyl)ethane (1 equiv.), potassium carbonate (4.5 equiv.), and 18-crown-6 (0.3 equiv.) in acetone was heated at reflux and stirred vigorously under nitrogen for 72 h. The mixture was allowed to cool, added to water and extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$ ). The combined extracts were dried over  $\text{MgSO}_4$  and evaporated to dryness. The crude product was purified as outlined in the following text.

**Dendrimer 1.** This was prepared from Fc-G0-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:4 ethyl acetate–hexane, to give dendrimer **1** (58%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 6H,  $\text{CH}_2$ ), 2.11 (s, 3H,  $\text{CH}_3$ ), 2.51 (t, 6H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.95 (t, 6H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.05 (m, 6H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 6H,  $\text{C}_5\text{H}_4$ ), 6.79 (d, 6H,  $J$  = 8.7 Hz, core Ar'H), 6.99 (d, 6H,  $J$  = 8.71 Hz, core Ar'H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.92 ( $\text{CH}_2$ ), 30.50 ( $\text{CpCH}_2$ ), 30.73 ( $\text{CH}_3$ ), 50.54 ( $\text{CCH}_3$ ), 67.15 ( $\text{CH}_2\text{O}$ ), 67.17, 68.03, ( $\text{C}_5\text{H}_4$ ), 68.46 ( $\text{C}_5\text{H}_5$ ), 88.25 ( $\text{C}_5\text{H}_5$ ), 113.60, 129.56, 141.71, 156.92 (Ar'C).

**Dendrimer 2.** This was prepared from Fc-G1-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:1 chloroform–hexane to give dendrimer **2** (57%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.98 (m, 12H,  $\text{CH}_2$ ), 2.11 (s, 3H,  $\text{CH}_3$ ), 2.51 (t, 12H,  $J$  = 7.8 Hz,  $\text{CpCH}_2$ ), 3.95 (t, 12H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.05 (m, 12H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 12H,  $\text{C}_5\text{H}_4$ ), 4.95 (s, 6H,  $\text{CH}_2\text{O}$ ), 6.42 (t, 3H,  $J$  = 2.0 Hz, ArH), 6.58 (d, 6H,  $J$  = 2.0 Hz, ArH), 6.87 (d, 6H,  $J$  = 8.7 Hz, core Ar'H), 7.00 (d, 6H,  $J$  = 8.7 Hz, core Ar'H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.47 ( $\text{CpCH}_2$ ), 30.76 ( $\text{CH}_3$ ), 50.60 ( $\text{CCH}_3$ ), 65.37 ( $\text{CH}_2\text{O}$ ), 67.21 ( $\text{C}_5\text{H}_4$ ), 67.30 ( $\text{CH}_2\text{O}$ ), 68.08 ( $\text{C}_5\text{H}_4$ ), 68.49 ( $\text{C}_5\text{H}_5$ ), 70.01 ( $\text{CH}_2\text{O}$ ), 88.16 ( $\text{C}_5\text{H}_4$ ), 100.77, 105.76, 113.95, 129.59, 139.35, 142.00, 156.80, 160.36 (Ar and Ar'C).

**Dendrimer 3.** This was prepared from Fc-G2-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:2 chloroform–hexane to give dendrimer **3** (59%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.97 (m, 24H,  $\text{CH}_2$ ), 2.11 (s, 3H,  $\text{CH}_3$ ), 2.50 (t, 24H,  $J$  = 8.1 Hz,  $\text{CpCH}_2$ ), 3.95 (t, 24H,  $J$  = 6.3 Hz,  $\text{CH}_2\text{O}$ ), 4.05 (m, 24H,  $\text{C}_5\text{H}_4$ ), 4.08 (m, 24H,  $\text{C}_5\text{H}_4$ ), 4.10 (s, 60H,  $\text{C}_5\text{H}_5$ ), 4.95 (s, 18H,  $\text{CH}_2\text{O}$ ), 6.42 (t, 6H,  $J$  = 2.0 Hz, ArH), 6.57 (m, 15H, ArH), 6.68 (d, 6H,  $J$  = 2.0 Hz, ArH), 6.87 (d, 6H,  $J$  = 8.7 Hz, core Ar'H), 7.02 (d, 6H,  $J$  = 8.7 Hz, core Ar'H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.84 ( $\text{CH}_2$ ), 30.44 ( $\text{CpCH}_2$ ), 50.72 ( $\text{CCH}_3$ ), 67.18 ( $\text{C}_5\text{H}_4$ ), 67.24 ( $\text{CH}_2\text{O}$ ), 68.06 ( $\text{C}_5\text{H}_4$ ), 68.46 ( $\text{C}_5\text{H}_5$ ), 69.83, 70.01 ( $\text{CH}_2\text{O}$ ), 88.10 ( $\text{C}_5\text{H}_4$ ), 100.81, 101.45, 105.73, 106.37, 113.89, 129.57, 139.38, 141.98, 156.69, 160.01, 160.30 (Ar and Ar'C).

**Dendrimer 4.** This was prepared from Fc-G3-Br and purified by column chromatography ( $\text{SiO}_2$ ), eluting with 1:2 chloroform–hexane to give dendrimer **3** (41%) as an orange solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.96 (m, 48H,  $\text{CH}_2$ ), 2.09 (s, 3H,  $\text{CH}_3$ ), 2.49 (m, 48H,  $\text{CpCH}_2$ ), 3.93 (t, 48H,  $\text{CH}_2\text{O}$ ), 4.05 (m, 96H,  $\text{C}_5\text{H}_4$ ), 4.10 (s, 120H,  $\text{C}_5\text{H}_5$ ), 4.94 (s, 36H,  $\text{CH}_2\text{O}$ ), 6.41 (m, 12H, ArH), 6.57 (m, 33H, ArH), 6.68 (d, 18H,  $J$  = 2.0 Hz, ArH),

6.87 (d, 6 H,  $J = 8.7$  Hz, core Ar'H), 7.01 (d, 6 H,  $J = 8.7$  Hz, core Ar'H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.89 ( $\text{CH}_2$ ), 30.47 ( $\text{CpCH}_2$ ), 67.21 ( $\text{C}_5\text{H}_4$ ), 67.33 ( $\text{CH}_2\text{O}$ ), 67.71 ( $\text{CH}_2\text{O}$ ), 68.08 ( $\text{C}_5\text{H}_4$ ), 68.28 ( $\text{CH}_2\text{O}$ ), 68.49 ( $\text{C}_5\text{H}_5$ ), 70.10 ( $\text{CH}_2\text{O}$ ), 100.89, 105.79, 106.40, 113.92, 138.94, 160.10, 160.36, 160.48 (Ar and Ar'C).

### Electrochemical apparatus

Electrochemical measurements were carried out with a BAS 100B/W Electrochemical Workstation. The working electrode for cyclic voltammetry and normal pulse voltammetry was a platinum disk electrode (0.5  $\mu\text{m}$  diameter, sealed in soft glass) that was polished prior to use with 1  $\mu\text{m}$  diamond paste and rinsed thoroughly with water and acetone. For coulometry a large platinum gauze electrode was employed. All potentials are referenced to the  $\text{Ag}/\text{Ag}^+$  (0.01 mol  $\text{dm}^{-3}$   $\text{AgNO}_3$ , 0.1 mol  $\text{dm}^{-3}$  TBAPF<sub>6</sub>– $\text{CH}_3\text{CN}$ ) reference electrode. A coiled platinum wire was used as a counter electrode and the electrochemical cells were of conventional design.

## Results and Discussion

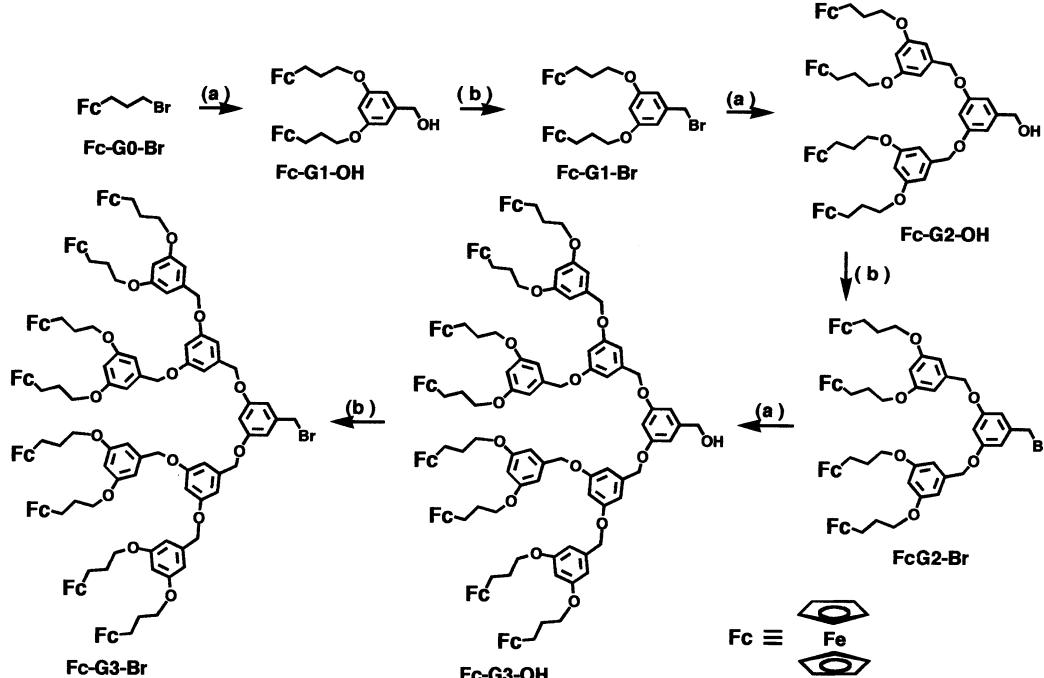
### Synthesis of dendritic macromolecules

A series of poly(aryl ether) dendrimers containing ferrocene functional groups located at the peripheries of their dendritic structures were prepared using the convergent approach developed by Hawker and Fréchet.<sup>7</sup> The synthetic route to the ferrocene-terminated dendritic wedges is illustrated in Scheme 1. This was made on the base of the Williamson ether synthesis for the formation of aryl ether from phenol and benzylic bromide (or alkyl bromide). We used 3,5-dihydroxybenzyl alcohol as the monomer unit. The ferrocene groups were introduced to the peripheries of the growing dendrimers by coupling two molecules of 3-bromopropyl ferrocene Fc-G0-Br to the phenolic groups of the monomer unit in the presence of potassium carbonate and 18-crown-6 in refluxing acetone, thereby obtaining the first generation alcohol Fc-G1-OH. We selected  $\gamma$ -propylferrocene as the terminal group because bromomethylferrocene, which is an  $\alpha$ -functional ferrocene derivative, is hydrolytically unstable and readily converted to ferrocenemethanol, and 2-bromoethylferrocene undergoes elimination during the alkylation reaction, producing vinylfer-

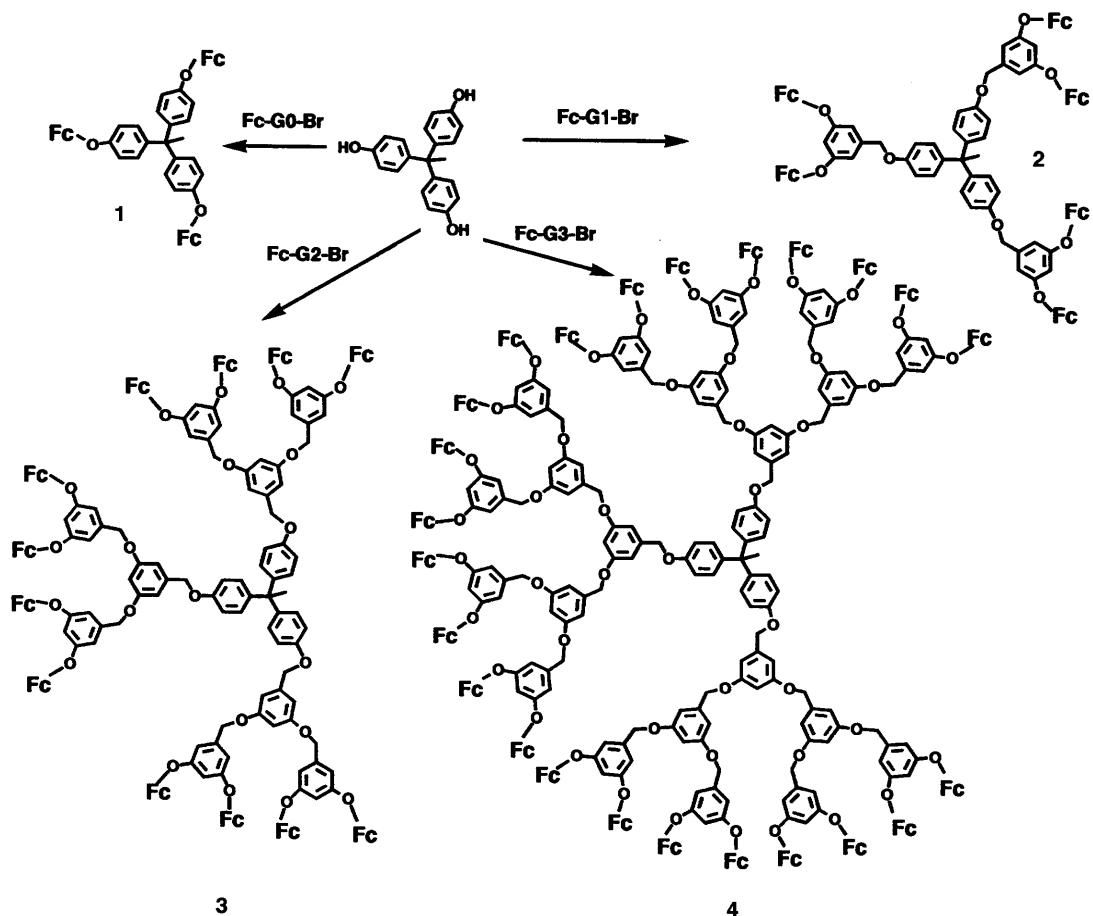
rocene. The bromide Fc-G0-Br was obtained by bromination of 3-ferrocenylpropanol, which was prepared according to the literature procedures.<sup>9</sup> Bromination of Fc-G1-OH with  $\text{PBr}_3$  restored the reactive bromomethyl functionality at the focal point of the dendritic wedge to give the corresponding benzyl bromide Fc-G1-Br. Reaction of Fc-G1-Br with 3,5-dihydroxybenzyl alcohol resulted in the formation of the next-generation benzyl alcohol Fc-G2-OH, and subsequent bromination of Fc-G2-OH with  $\text{PBr}_3$  gave the second generation bromide Fc-G2-Br. Repeated alkylation and bromination led to the third generation alcohol Fc-G3-OH and the bromide Fc-G3-Br. In the convergent approach, the dendritic wedges obtained are attached to a polyfunctional core. The polyfunctional core we chose was 1,1,1-tris(4-hydroxyphenyl)ethane. Coupling reactions of the phenolic groups of the core molecule with each bromide generation, from Fc-G0-Br to Fc-G3-Br, as shown in Scheme 2, were carried out. Thus, a family of dendritic poly(arylether)s, dendrimers **1**, **2**, **3** and **4**, containing 3, 6, 12 and 24 ferrocene functionalities, respectively, at their peripheries were obtained. The products were purified by column chromatography, and their purities were evaluated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. No signal of the starting materials was detected in the NMR experiments.

### Characterization

The ferrocene-terminated dendrimers were characterized structurally using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.  $^1\text{H}$  NMR spectroscopy is particularly crucial in confirming the structures produced by our synthetic strategy.  $^1\text{H}$  NMR spectra showed the exterior functional group gave five sets of resonances at  $\delta$  4.10 ( $\text{C}_5\text{H}_5$ ), 4.08, 4.05 ( $\text{C}_5\text{H}_4$ ), 3.95 ( $\text{CH}_2\text{O}$ ), 2.50 ( $\text{CpCH}_2$ ) and 1.98 ( $\text{CH}_2$ ). This result is consistent with the expected highly symmetrical structures of the ferrocene dendrimers. The resonances for the aromatic protons of the internal 3,5-dihydroxybenzyl group occurred in the  $\delta$  6.50–6.70 region. All benzylic protons resonate at  $\delta$  4.91–5.02, except those at the focal point at which  $\text{CH}_2\text{OH}$  appears at  $\delta$  4.62 and  $\text{CH}_2\text{Br}$  at  $\delta$  4.42. Changes in resonance of benzylic protons occurred upon conversion of the dendritic alcohol to the corresponding bromide, and on attachment of the bromide to the polyfunctional core, were used to monitor product purities. When



**Scheme 1** Reagents and conditions: (a) 3,5-dihydroxybenzyl alcohol,  $\text{K}_2\text{CO}_3$ , 18-crown-6, reflux in acetone; (b)  $\text{PBr}_3$ ,  $\text{C}_6\text{H}_6$ , room temperature



Scheme 2

dendritic wedges were attached to the core molecule 1,1,1-tris(4-hydroxyphenyl)ethane, two doublets of the aromatic rings of the core moiety were observed at  $\delta$  6.87 and 7.02, and were not obscured by the aromatic resonances of the dendritic wedges; the methyl group of the core resonated at  $\delta$  2.11. Integration data for the exterior ferrocene groups, the internal aromatic groups, and the aromatic rings of the core moiety confirmed the structures and the generation numbers of the dendrimers. The  $^{13}\text{C}$  NMR spectra provided further support for the structural assignments. Each of the different carbon resonances was found to agree with the observed spectral resonances.

### Electrochemistry

Electrochemistry studies of the ferrocene dendrimers in  $\text{CH}_2\text{Cl}_2$  solutions containing  $0.1 \text{ mol dm}^{-3}$  TBAPF<sub>6</sub> as the supporting electrolyte were performed. Cyclic voltammograms of **1** and **2** show the characteristics of a reversible one-electron oxidation, with production of soluble, stable cations. However, with **3** and **4**, a stripping peak appeared on scan reversal. The shape of the reduction peak indicated that the oxidized products were insoluble and accumulated on the electrode's surface. The precipitation problems led us to use the normal pulse voltammetry (NPV) technique, which is less susceptible to problems of adsorption and precipitation as a means of determining the wave parameters.<sup>13</sup> The normal pulse voltammograms of **3** in  $\text{CH}_2\text{Cl}_2$  are shown in Fig. 1A. Surprisingly, the slope of  $E$  vs.  $\log(i_d - i)/i$  plot, where  $i_d$  is the limiting diffusion current, obtained from the normal pulse voltammogram is 42 mV, which is different from the slopes (60 mV) reported for most polymers (or dendrimers) containing multiple ferrocenyl moieties.<sup>13–15</sup> We speculated that the reason why a value of 42 mV was obtained instead of 60 mV may be due to severe adsorption

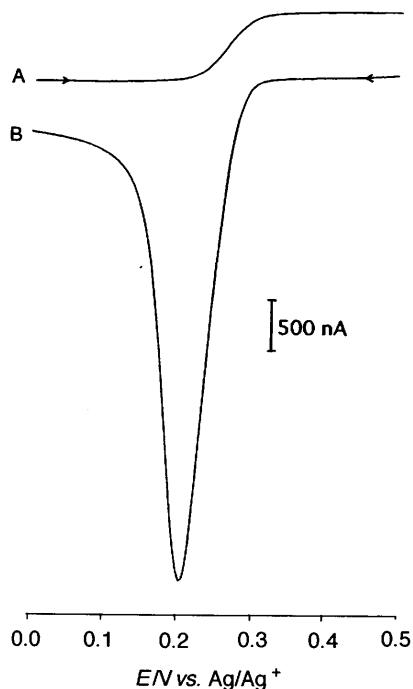


Fig. 1 Normal pulse voltammograms for  $50 \mu\text{mol dm}^{-3}$  of dendrimer **3** in  $0.1 \text{ mol dm}^{-3}$  TBAPF<sub>6</sub>– $\text{CH}_2\text{Cl}_2$ . A, Potential scanned in the forward direction, initial potential 0 mV vs.  $\text{Ag}/\text{Ag}^+$ ; B, potential scanned in the reverse direction, initial potential 500 mV vs.  $\text{Ag}/\text{Ag}^+$ . Scan rate 20 mV s<sup>–1</sup>; sample width 17 ms; pulse width 50 ms.

of the oxidized product. The effects of absorbed reactants and products on the plateau currents and half-wave potentials in normal pulse voltammograms have been reported by Anson *et al.*<sup>16</sup> In the absence of an independent determination, it is difficult to deduce the presence of product adsorption from normal pulse voltammograms. However, the appearance of a peak current in the voltammogram recorded in the reverse-scan direction verifies the occurrence of adsorption. Indeed, for dendrimer **3** there is a peak current recorded in the reverse-scan voltammogram, as shown in Fig. 1B.

In order to reduce perturbations in the shape of normal pulse voltammograms induced by adsorption, we used a mixed solvent, 3:5 CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> in the electrochemical studies, where the adsorption of the dendrimers and their oxidized products was minimized. Fig. 2 shows the cyclic voltammogram of the ferrocene-terminated dendrimers in the mixed solvent containing 0.1 mol dm<sup>-3</sup> TBAPF<sub>6</sub> as the supporting electrolyte. The cyclic voltammogram of each dendrimer exhibits a single reversible oxidation wave corresponding to oxidation of the exterior ferrocene groups. The peak current is linearly proportional to the square root of the scan rate, the peak shape is symmetrical, with  $i_{pc}/i_{pa} \approx 1$ , and  $E_p$  is independent of the scan rate. The peak potential separation  $\Delta E_p$  is ca. 59 mV for dendrimers **1** and **2**, 52 mV for **3** and 50 mV for **4**. The smaller  $\Delta E_p$  values for dendrimers **3** and **4** may be attributable to minor adsorption of the dendrimers (or oxidation products) on the electrode surface. The half-wave potentials ( $E_{1/2}$ ) and  $\Delta E_p$  obtained from the cyclic voltammograms are given in Table 1. Note that the sharp anodic or cathodic peak current due to the adsorption of reactant or product is not observed in the mixed solvent system. The electrochemical properties of the dendrimers were also studied using the NPV

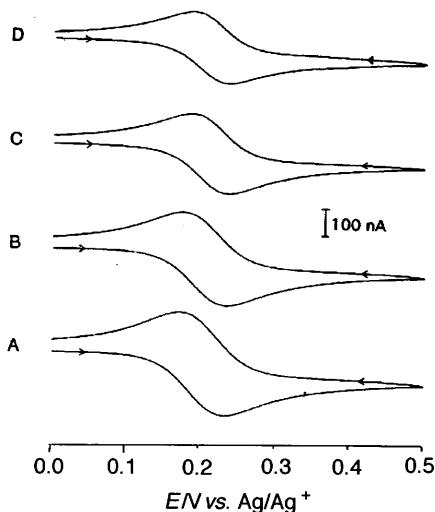


Fig. 2 Cyclic voltammograms for A, 200  $\mu\text{mol dm}^{-3}$  of **1**; B, 100  $\mu\text{mol dm}^{-3}$  of **2**; C, 50  $\mu\text{mol dm}^{-3}$  of **3**; and D, 25  $\mu\text{mol dm}^{-3}$  of **4** in 0.1 mol dm<sup>-3</sup> TBAPF<sub>6</sub>–3:5 CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub>. Scan rate 60 mV s<sup>-1</sup>.

Table 1 Results of cyclic voltammetry, normal pulse voltammetry and controlled-potential electrolysis for the oxidation of ferrocene-terminated dendrimers **1**–**4**<sup>a</sup>

compound	$E_{1/2}^b$ /mV	$E_{1/2}^c$ /mV	$\Delta E_p$ /mV	slope <sup>d</sup> /mV	$i_d \times 10^{-1}$ $\mu\text{A}$	$Q_c \times 10^{-1}$ C	$n_p^f$
<b>1</b>	211	208	59	60	8.16	2.90 (0.03)	3.0 (0.1)
<b>2</b>	211	208	59	58	7.21	2.95 (0.03)	6.1 (0.1)
<b>3</b>	213	212	52	56	5.90	2.74 (0.06)	11.4 (0.2)
<b>4</b>	214	212	50	58	5.14	2.70 (0.05)	22.4 (0.4)

<sup>a</sup>Experimental conditions are given in the captions to Fig. 2 and 3. <sup>b</sup>By cyclic voltammetry. <sup>c</sup>By normal pulse voltammetry. <sup>d</sup>Slope of plot of  $E$  vs.  $\log(i_d - i)/i$ . <sup>e</sup>The electrolysis solutions were 5 ml, and the concentration of each solution was as indicated in the captions to Fig. 2 and 3. Values are an average of three independent determinations, and standard deviations are listed in parentheses. <sup>f</sup>Number of ferrocenes per molecule oxidized.

technique. Normal pulse voltammograms of the dendrimers are displayed in Fig. 3. The half-wave potentials, limiting diffusion currents ( $i_d$ ), and slopes of  $E$  vs.  $\log(i_d - i)/i$  plots, obtained from the normal pulse voltammograms are given in Table 1. The  $E_{1/2}$  values, as determined by NPV, are similar to those determined by cyclic voltammetry. Interestingly, the  $E_{1/2}$  values for the ferrocene redox couples remain essentially constant upon successive generation buildup. This can be explained by noting that the ferrocene functional groups are located on the outer surfaces of the dendrimers and their microenvironments are independent of dendrimer generation. This result is in contrast to the recent observation by Diederich *et al.*<sup>17</sup> that for zinc porphyrin dendrimers the redox potential shifts as generations build up. Because the redox group is located in the interior of the porphyrin macromolecules, the electrophore environment, as well as the redox potential of the zinc porphyrin, changes markedly with increasing generational cascading. It was observed that oxidation of the terminated ferrocenyl units in the dendrimers occurred at a potential *ca.* 40 mV more negative than the corresponding process in ferrocene. This was due to the electron-donating effect of the alkyl group on the ferrocenyl moiety, making the chain-end ferrocenyl groups more easily oxidized. For the dendrimers, the values of  $\Delta E_p$  determined from CV and the values of slopes obtained from NPV are close to the theoretical value of 59 mV for a reversible one-electron transfer reaction, indicating that all the ferrocenyl redox centres located at the peripheries of

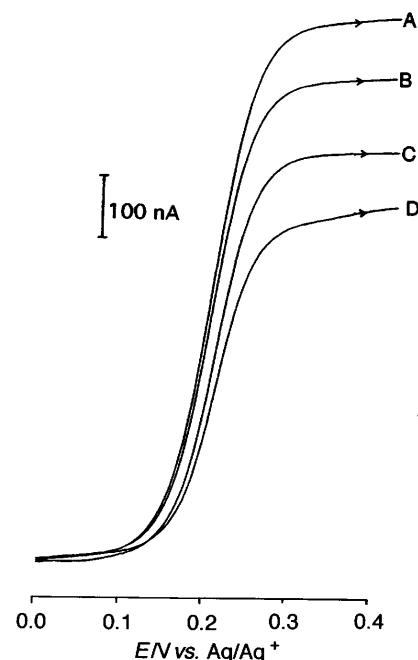


Fig. 3 Normal pulse voltammograms for the oxidation of A, 200  $\mu\text{mol dm}^{-3}$  of **1**; B, 100  $\mu\text{mol dm}^{-3}$  of **2**; C, 50  $\mu\text{mol dm}^{-3}$  of **3**; and D, 25  $\mu\text{mol dm}^{-3}$  of **4** in 0.1 mol dm<sup>-3</sup> TBAPF<sub>6</sub>–3:5 CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub>. Scan rate 20 mV s<sup>-1</sup>; sample width 17 ms; pulse width 50 ms.

these dendrimers are equivalent, non-interacting and exchange electrons with the electrode in waves characteristic of one-electron transfer processes.

To evaluate the total number of electrons transferred during oxidation without knowing the relative diffusion coefficients, controlled-potential electrolyses were carried out. Coulometric oxidation of the dendrimers was performed at a large-area platinum gauze electrode in a  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{CN}$  mixture at  $E_{\text{app}}$  150 mV more positive than the respective anodic potential. The results are given in Table 1. It is shown that values of  $n_p$ , the number of electrons per molecule consumed in the oxidation, calculated from the total number of coulombs, come close to matching the number of ferrocenyl groups anticipated in the synthetic strategy bound to the chain-ends of these dendrimers. Note that the values of  $n_p$  obtained for **3** and **4** are somewhat smaller than the number of ferrocene groups attached to these dendrimers. This may have been because the rate of electrolysis of dendrimers **3** and **4** slowed drastically near the end of coulometric oxidation, and at the time the controlled-potential electrolysis was stopped, the ferrocene redox groups that were bound to the dendrimers in the solution were not totally oxidized.

## Conclusion

Using the stepwise convergent approach we have synthesized a series of dendritic poly(aryl ether)s that contain 3, 6, 12 and 24 ferrocene functionalities located exclusively at the peripheries of their dendritic structures. The structures of these dendrimers were characterized using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The results of electrochemical studies show that electron transfers from the dendritic macromolecules yielded voltammetric waves with shapes matching those of corresponding molecules with electroactive centres, but with magnitudes determined by the total number of redox centres present. On the basis of this observation, we conclude that the ferrocenyl moieties located on the outer surfaces of these dendrimers are non-interacting redox centres, are electrochemically equivalent and oxidizable at the same potential. This fully reversible multi-electron redox system may be useful for multi-electron redox catalysis.

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